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# Automated Chemical Process Control System

## Relationship to Other Application

This application claims the benefit, and is a continuation-in-part, of U.S. Provisional Application No. 60/081,240 filed April 9, 1998.

## Background of the Invention

### FIELD OF THE INVENTION

This invention relates generally to chemical processing systems, and more particularly, to a system that monitors and replenishes automatically a liquid volume in a chemical processing system, such as a chemical bath. In addition, the invention described herein relates to an automatic on-line chemical bath control system which, for example can be used as an automatic chemical bath control system for a chemical mechanical planarization processes.

### DESCRIPTION OF THE RELATED ART

Chemical mechanical planarization or polishing (CMP) processes are widely used in the manufacture of microcircuits. A typical CMP process utilizes a slurry of an abrasive in a diluent, which is, in some cases, an oxidizer. Maintaining the slurry quality is essential to maximizing device yields. Dynamic measurements of slurry properties, such as pH, specific gravity, percent solids by weight, or slurry particle size distribution, should be made to ensure the that the slurry is stable. That is, the slurry must be resistant to settling and agglomeration, and be free of contaminants, such as slurry particle aggregates, foreign particles, adsorbed carbon dioxide, and ionic contaminants.

Monitoring and measuring of the slurry properties and chemical component assays can be done on-line, or off-line. While on-line measurements provide real-time data, many analytical instruments are not easily adapted to on-line sampling thereby causing users to opt for off-line analytical techniques. In addition, on-line analytical instruments require frequent maintenance and calibration for proper operation. There is, therefore, a need in the art for improved automatic on-line CMP process control.

One of the most difficult aspects to control in current CMP processes is the mechanical action. As circuits become more miniaturized, mechanical action is too coarse and difficult to control to the fine resolution required. Therefore, new CMP processes are under development which rely to a greater extent on chemical polishing,

rather than mechanical polishing. However, chemical polishing requires even greater control of the chemical bath since many of the chemicals being added are dynamic in nature and are depleted by use, particularly in the case of hydrogen peroxide, which decomposes over time and also varies in supplied feedstock concentration. This variation and decomposition affects both, the makeup (blending) and distribution (or holding) stages of CMP slurry preparation and usage. The only way to control properly the chemical bath is through frequent and accurate chemical analysis and replenishment.

In addition to the foregoing, chemical components of a CMP chemical bath should be monitored and replenished, as required. As an example, Semi-Sperse® W2000, a tungsten CMP slurry manufactured by Cabot Corporation, Aurora, IL, is a non-metal based slurry that, when mixed with an oxidizer, is useful for polishing tungsten and titanium. However, the oxidizer (hydrogen peroxide) concentration must be monitored and replenished. Ideally, monitoring and replenishment should be on-line and automated. Weight percent of hydrogen peroxide in Semi-Sperse® W2000 can be tested using reduction titration with an oxidizing agent such as cerium sulfate ($Ce(SO_4)_2$) or potassium permanganate ($KMnO_4$). However, in order to be useful, an automated titration/control system must be as or more reliable, accurate, and repeatable than manual titration methods. For this, platinum ORP, gold ORP, thermometric, or colorimetric sensors may be used to detect a differential endpoint (*i.e.*, the inflection point). There is therefore a need in the art, for accurate, reliable and repeatable in-line analysis of chemical CMP baths and automated replenishment of depleted bath components.

## Summary of the Invention

### Objects of the Invention

It is, therefore, an object of this invention to provide a chemical analysis and control system that protects the process under control from spurious results.

It is another object of this invention to provide a chemical control system that achieves accurate and variable water and reagent delivery.

It is also an object of this invention to provide a chemical analysis system that effects continuous titration vessel level sensing.

It is a further object of this invention to provide a chemical analysis system that achieves automated detection of problems related to titration vessel level changing, such as insufficient reagents, low water pressure, or inoperative valves.

It is additionally an object of this invention to provide a chemical analysis and control system that alerts a user to potential problems in the system that would require, for example, cleaning or preventative maintenance.

It is yet a further object of this invention to provide a chemical analysis system that provides to the user an indication of changes in the day-to-day performance of the system.

It is also another object of this invention to provide a chemical analysis system that automatically and safely replenishes a predetermined volume of a chemical.

It is yet an additional object of this invention to provide a chemical analysis system that achieves minimal water consumption during cleaning and filling of a titration container.

It is still another object of this invention to provide a chemical analysis system that achieves continuous level measurement of a broad range of corrosive and caustic solutions in a confined space.

It is a yet further object of this invention to provide a chemical sampling system that can draw a representative chemical sample from a static tank several hundred feet away and achieve accurate, repeatable measurements of the chemical characteristics of the drawn sample.

It is also a further object of this invention to provide a chemical sampling system that can draw a representative chemical sample from a static tank several hundred feet away without requiring installation and operation of a pump at the tank that would create a further recirculating loop.

It is additionally another object of this invention to facilitate accurate makeup (blending) of peroxide slurry and othermixtures by analyzing and compensating for feedstock supply variation and decomposition.

A still further object of this invention is to provide prevent wastage of the unused chemical under test by providing the ability to restore same to the tank from which it was drawn.

An additional object of this invention is to provide a chemical analysis system that accommodates a wide range of sample volumes and concentrations, thereby increasing system versatility.

Yet another object of this invention is to provide a chemical analysis system that provides a reference cell having an extended term zero potential electrical connection to the solution, without suffering the ion migration problems associated with a gel-filled reference cell electrolyte, or the use of a flow-limiting, electrolyte preserving, plug of porous wood, ceramic, or plastic installed at the tip.

Another object of this invention is to provide a chemical processing system that accurately maintains the concentration of blended and held mixtures by measuring the level of the mixtures and calculating their respective volumes, then adjusting replenishment quantities that have been determined by analysis, or in response to the passage of time, in response to solution tank volumes.

Still another object of this invention is to provide a chemical control system wherein there is provided level monitoring, chemical analysis, and peroxide control in blend and distribution (or hold) tanks used in CMP slurry preparation.

An object of this invention is to provide a chemical processing system having electronic communication of data containing information related to analysis results, status, errors, replenishment quantities, *etc.* with a remote host operator interface.

### General Introduction to the System of the Present Invention

The foregoing and other objects are achieved by this invention which provides, in a titration analyzer embodiment of the present invention, a microprocessor-based system that performs a variety of wet chemical analysis procedures, such as direct pH measurement or pH, ORP or colorimetric titrations. The analyzer of the present invention also performs sample retrieval, sample preparation, cleanup, data manipulation, auto-calibration, and diagnostics.

Once an analysis is initiated by an automated manager portion of the system, which may be implemented in a personal computer, the analyzer performs a series of tests without the need for further instruction by a human operator. Each analysis is automatically replicated and the results of the analyses are statistically evaluated to assure the final reported result is repeatable to within a user-specified tolerance. The final result is then validated by the computerized manager by performance of a series of range and trend checks.

The computerized manager enables the user to view and modify analysis configuration parameters, such as sample volume, dilution volume, and tolerance. Additionally, the computerized manager affords the user has the flexibility to operate the various valves, syringes, and mixer(s), and to obtain electrode and detector readings. These devices will be described in detail below.

In accordance with one aspect of the invention, an on-line automatic analyzer eliminates the need for manual analysis and provides analytical accuracy and repeatability that surpasses manual methods and conventional instruments. The inventive system operates, in some embodiments of the invention, in combination with a replenishment system, whereby control over process baths, as well as the monitoring thereof, are automated.

The analyzer of the present invention draws samples automatically from multiple process baths and performs chemical analysis of the process chemistries. The results of the analysis are delivered to a manager system. Self calibration and diagnostic routines are programmed within the analyzer to ensure consistent and reliable system performance.

As indicated, the analyzer of the present invention includes a precision replenishment system that receives chemical addition instructions from the manager system. In accordance with the invention, the chemical addition instructions are based on analytical results, amp-minutes, process time (time in bath), or on manually entered operator commands. The manager system identifies to the replenisher control system the particular pump to be activated, and the particular valve that will be opened or closed. Precision flow sensors are used to monitor the volume being added. The system is

designed to maintain inventories of chemical stocks and report on chemical usage by process batch. A digital keypad is employed to enable remote control over the system operation.

In one embodiment of the invention, the PC interface is a MICROSOFT Windows®-based system that employs graphical icons to simplify operation of the system. The computerized manager communicates with all of the other modules that will be described herein via an RS-422 interface, and processes incoming data according to predetermined operator settings. Commands issued by the computerized manager initiate control functions and operator alarms. In a further embodiment of the invention, the computerized manager includes a database that provides a history of all parameters monitored by the system. Such historical information can be used to generate reports that are available from the computerized manager. Thus, at any time, for any time frame, and for any parameter, bath, chemical, or module, an operator can print a variety of tables, graphs, charts, and status reports.

SUMMARY OF THE PRINCIPLES OF OPERATION

The analyzer of the present invention performs three basic functions, specifically sampling, analysis, and cleanup. Included in these functions are diagnostics, auto-calibration, and calculations.

*SAMPLING*

Sampling retrieves liquid from a tank, sample loop, or grab sample receptacle and delivers it to the analysis cell. For titrations and/or analyses where an exact quantity of sample is required, a sample syringe is cycled to pump the sample in and purge any other liquid. Several cycles of sample are delivered to the reaction cell beaker to ensure that the sample is representative of the liquid in the tank. During this phase, both a timer and a sample arrival detector are used to verify that the sample arrived within an adequate period of time for the analysis to proceed. The beaker is thoroughly cleaned before the final sample dose is dispensed. For analyses where the sample is tested directly, without any dilution, the liquid either is pushed into the analysis beaker by the pressure in the sample loop or drawn in by an eductor.

*ANALYSIS*

Analysis is performed after the sample has been delivered to the cell. A titration analysis may be performed with an optional conditioning reagent delivered, in one embodiment of the invention, by gravity through a solenoid valve. Titrant is conveyed by a syringe that is actuated under the control of a stepper motor. Titrant is continuously added while analog readings are taken at predetermined intervals in order to find the endpoint. Once the endpoint is found, the beaker is cleaned and the test is repeated until the results agree within a user-specified tolerance. In a practicable embodiment of the invention, a minimum of three replicates is required, with a maximum of nine being permitted. As soon as the results are satisfactory for non-continuous analyses, the analyzer performs a thorough cleanup to avoid cross contamination.

*CLEANUP*

The cleanup procedure rinses out all the analyzer components that came in contact with the sample solution. This starts with an air purge through the rotary valve(s) and filters. If the sample fails to clear through the line, an error condition is generated for subsequent analyses warning that the air pressure is low. Once cleared by air, the rinse water, in the form of bursts to maximize the rinsing effect, is turned on, and if used, the sample syringe is cycled until it is cleaned. Depending upon the process for which the analyzer is being used, there may not be a water rinse of the sampling lines. Following this, the direct fill line to the beaker is cleared.

*GRAB SAMPLE*

Bottled samples may be presented to the analyzer for analysis at the grab sample sipper port. For optimum results the sample concentration should be within the specification range (alarm limits) of the parameter being tested.

*PH ELECTRODE CALIBRATION*

The pH calibration is performed before an analysis using the pH electrode if a user specified time has elapsed since the last pH calibration. The calibration uses two pH buffers to determine the slope and the offset of the pH electrode. A stable reading is obtained on one buffer, then the beaker is cleaned and a reading is taken on the other. The slope value is transmitted to the automated manager to enable the operator to know the condition of the electrode. The slope and offset values are retained by the analyzer

to convert voltage readings to pH values. The frequency of calibration is set through the analysis configuration table register titled "Hours calibration valid."

### *ORP Electrode Calibration*

Because the ORP electrode is used for differential rather than absolute titrations, calibration is unnecessary. However, determining the sensitivity of the electrode is desirable since it can vary with use. Electrode sensitivity, calculated as a ratio of actual response to ideal response, is reported after each analysis and can be viewed at the automated manager with the other analyzer parameters.

### *ISE Methodology and Calibration*

Ion selective electrodes (ISE) are used to measure a variety of analytes using the method of standard addition. In the method of standard addition, known amounts of a standard solution having a known concentration of analyte are added sequentially to a solution of unknown concentration. The electrode potential is measured after each addition. The increased signal produced by an ion selective electrode permits determination of the quantity of analyte in the original sample by extrapolation back to the point of zero analyte concentration.

Three to five such additions are made so as approximately to double the concentration with each addition. In this way the potential change between additions, $\Delta E$, is large enough to give precise results. About a 20 mV change or more is preferable and should never be less than 5 mV. The larger the value of DE, the more repeatable the analysis becomes. A high concentration of standard is also best so as to minimize diluting the test solution. (An ion selective electrode is also sensitive to solution ionic strength.)

The method of standard addition is accurate and reproducible. It avoids the requirement of preparing calibration standards having a background solution (matrix) identical to that of the unknown. The underlying assumption in using a standard (known) addition is that the matrix has the same effect on added analyte as it has on the original analyte in the unknown sample.

### *Turbidity Probe Methodology and Tuning*

The turbidity sensor is used to measure 1) concentrations that are proportional to turbidity and 2) titrations that have turbid (cloudy) endpoints. The proportional method requires calibration to establish the correlation between turbidity and concentration. Sulfate measurement (in the form of barium sulfate) is an example this type of measurement.

An example of a turbid endpoint titration is that used for cyanide in plating solutions. The method is to titrate a solution of unknown cyanide concentration with silver nitrate. When all of the cyanide has been consumed with silver ion, additional silver ion combines with iodide indicator to form a cloudy precipitate in the beaker. This cloud is detected by the turbidity sensor, signaling the endpoint of the titration. Graphically this increase in turbidity appears as an elbow or sudden bend upward in the turbidity.

For the endpoint method, the turbidity probe does not require calibration except possibly when the probe is replaced. This is due to the fact that the titration is looking for a relative change and not an absolute value. The resistors associated with the probe are set so as to provide ample sensitivity for detecting even a slight turbidity. By adjusting the detection value in analysis configuration table, the titration can be tuned to match what an operator would first observe as the endpoint. The endpoint detection can be set anywhere from nearly invisible turbidity to very cloudy.

## SUMMARY OF THE CLAIMED INVENTION

In accordance with a first system aspect of the present invention, there is provided a chemical control system for a chemical solution having predetermined chemical constituents. In accordance with this aspect of the invention, an analyzer determines the proportion of one of the predetermined chemical constituents in the solution. A precision analyzer sample delivery arrangement delivers to the analyzer a sample of the liquid chemical. Information relative to the determination by the analyzer of the proportion of at least one of the predetermined chemical constituents in the liquid chemical to be delivered is received by a controller. The controller may be implemented as a microcomputer. A replenisher that is responsive to the controller dispenses a controlled quantity of the predetermined chemical constituent. The controlled quantity of the

predetermined chemical constituent is delivered to a tank or container that holds the chemical solution.

In one embodiment of the invention, the analyzer is a titrater system. Certain characteristics of the sample are monitored by one or more sensors or electrodes in response to the addition of certain reagents.

The analyzer includes, in certain embodiments, a reaction cell for receiving a sample of the liquid chemical from the precision analyzer sample delivery arrangement. An electrode measures the predetermined electrical characteristic of the liquid chemical in a practical embodiment of the invention, the reaction cell is a glass beaker. The sensor may be any one or more of a pH electrode, a ORP electrode or an ion selective electrode, or a turbidity sensor.

The present invention is capable of monitoring a slurry. In such an embodiment, one of the predetermined chemical constituents in the slurry is $H_2O_2$. Chemical delivery is effected via a global loop that distributes the chemical solution in the plant. The global loop may be pressurized.

The aforementioned controller is provided with a display in certain embodiments for displaying information that is responsive to the determination made by the analyzer. In addition, the display may display information related to predetermined parameters of the chemical delivery system, diagnostic conditions of the chemical delivery system, a history of replenishment operations, a history of system faults, information relating to the calibration of the chemical sensors, the amount of chemical in the chemical distribution arrangement, as well as a plurality of additional system parameters and their history.

In a further embodiment, the liquid level in each source tank is monitored by monitoring the head pressure of a gas, such as $N_2$, that is delivered from a pressure regulator through an orifice, and out of a tube that is immersed in the source tank. The pressure of the monitoring gas past the orifice is responsive to the liquid chemical level. The pressure of the monitoring gas is maintained in nominally between approximately one and fifteen psi, and preferably between two and ten psi.

In a highly advantageous embodiment of the invention, the precision analyzer sample delivery arrangement includes an eductor for drawing a sample to the analyzer. The eductor creates a negative pressure in the sample line.

After each reading is recorded, the analyzer is cleared by a purge system. In one embodiment, the purge system includes a gas purge valve that controls the pressurized purge gas for clearing the analyzer. In addition, certain embodiments include a rinse solvent purge valve that controls the flow of a rinse solvent for clearing the analyzer. The rinse solvent may be arranged to clear the gas purge valve, in addition to the analyzer.

In accordance with a further system aspect of the invention, there is provided a chemical delivery system for a chemical solution having a predetermined chemical constituent. The chemical control system includes a precision analyzer sample delivery arrangement that delivers a sample of a precise quantum of the liquid chemical. The precise sample is received in a reaction cell, and a precise quantity of a predetermined reagent is delivered to the reaction cell by a precision analyzer reagent delivery arrangement. A sensor then measures a characteristic of the liquid chemical typically during the addition of a reagent. A controller then receives information relative to the actual characteristic of the liquid chemical measured by the sensor and stores same for subsequent analysis. The data is then used by the controller to control a replenisher that adds a controlled quantity of the predetermined chemical constituent to the source of the liquid chemical.

The sample of the chemical solutionis delivered to the reaction cell via a sample line, and there is provided a detection arrangement for detecting the presence of the liquid chemical in the line. In one embodiment, the sensor constitutes a proximity or optical sensor arranged near the sample line. This sensor, therefore, provides to the controller indication of the availability of the liquid chemical.

In a highly advantageous embodiment of the invention, the precision analyzer sample delivery arrangement constitutes a syringe. The syringe is operated by a controllable driver arrangement which includes a drive motor and controlled circuitry therefore. Preferably, the drive motor is of the known stepper type.

As previously noted, after the analysis of the chemical solution is completed, the reaction cell and the sample lines are cleared by a clean up arrangement that employs a purge gas. Additionally, the clean up arrangement employs a rinse solvent. The rinse solvent, which may be water is applied in certain embodiments of the invention in the form of bursts which maximize the rinsing effect. The clean up arrangement additionally cycles the sample syringe until it is cleared of the prior sample.

In accordance with a first method aspect of the invention, there is provided a method of analysis of the chemical solution in a tank having a first chemical composition. The method includes the steps of:

delivering a sample of the chemical solution having the first chemical composition to an analysis cell;

performing a titration analysis on the chemical solution having the first chemical composition that has been delivered to the analysis cell, said step of performing a titration analysis including the further steps of:

controlling a syringe to convey a titrant to the chemical solution having the first chemical composition that has been delivered to the analysis cell; and

analyzing a predetermined chemical characteristic of the chemical solution;

determining an end point of the titration analysis; and

conducting a cleanup procedure.

In one embodiment of this method aspect of the invention the step of delivering includes the further step of delivering a predetermined sample quantity of the chemical solution having the first chemical composition to the analysis cell. In a further embodiment, the step of delivering includes the step of varying a rate at which the step of performing a titration analysis is conducted. This step of varying is responsive to the step of determining an endpoint of the titration analysis. In a first phase, a titration analysis is conducted in inverse proportion to a rate of change of a monitoring signal. However, as the endpoint of the titration analysis is approached, the rate of delivery of titrant is changed. In essence, during an initial phase of titration, the titrant is delivered

at a maximum possible speed without delivering more than the reaction can consume and without overshooting the endpoint. However, as the endpoint is reached, as indicated by the increased degree of sensor change per unit volume of titrant added the system switches to a second phase. In the second phase, the rate of titrant addition is fixed and rather slow, and the sensor response is allowed to change freely through the inflection point. This is done to favor accuracy over speed since changing speed while near the endpoint has been found to affect or shift, the titration results somewhat.

In another embodiment of the invention the step of delivering includes the step of purging from a sample loop all liquid associated with a prior sample. In this manner, the subsequent sample to be delivered will be representative of the current content of the liquid chemical being distributed.

The step of delivering includes a further step of detecting the delivery of the sample of the chemical solution having the first chemical composition to the analysis cell. This step is effected as previously described using a proximity or optical sensor, in certain embodiments. Also, the delivery of the sample is timed. If the sample fails to become available within a predetermined maximum period of time, a false conditioned is announced.

In a still further embodiment of the invention, the step of performing a titration analysis includes the step of delivering a conditioning reagent. In some embodiments, such delivery of the conditioning reagent is effected via a controlled gravity feed arrangement.

The step of controlling a syringe to convey a titrant includes, in certain embodiments, controlling a stepper drive arrangement that is coupled to the syringe. The advantageous use of a syringe in the present invention permits precise control over the quantity of titrant or sample delivered to a reaction cell. Additionally, the use of a controlled stepper drive enables control over the rate of delivery.

In a still further embodiment of this method aspect of the invention, the steps of monitoring a predetermined chemical characteristic of the chemical solution and determining an endpoint of each titration analysis, are repeated. Such steps are repeated until it is determined that the result of the titration analysis is established within

predetermined parameters to be itself repeatable. In one embodiment, these steps are conducted approximately between three and nine times.

As previously indicated, after conducting the analysis, there is performed a step of conducting a clean up procedure that includes the step of forcing an air purge through a filter through which was flowed the chemical solution having the first chemical composition. All sample lines and the reaction cell are also purged, in certain embodiments. Additionally, the sample syringe is cycled until it is cleared of the prior sample. In one embodiment, the pressure of the purge gas is monitored, and an error warning is issued if such pressure falls below a predetermined pressure. Additionally, a rinse solvent which may be water, is caused to flow through the filter and the associated sample lines.

Prior to performing the step of performing a titration analysis, there is provided the step of calibrating a pH electrode. This step of calibrating a pH electrode includes the further steps of

taking a first pH reading with the pH electrode using a first pH buffer;

taking a second pH reading with the pH electrode using a second pH buffer; and determining slope and offset values for the pH electrode. In another embodiment, there is provided an ORP electrode. In this embodiment, the step of performing a titration analysis includes the step of performing a differential titration analysis. There additionally provided the step of determining the sensitivity of the ORP electrode.

In some embodiments, the determination of an endpoint of the titration analysis includes the step of determining a turbid endpoint. This includes the use of a turbidity sensor to determine the turbid endpoint of the titration. Usually, this embodiment includes the further step of titrating a solution of unknown cyanide concentration, and may employ a silver ion. The use of a turbidity sensor to determine to turbid endpoint of the titration additionally may include the step of determining a change in the rate of change of turbidity of the chemical solution.

In accordance with a further method aspect of the invention, there is provided a method of analysis of a chemical solution in a tank having a first chemical composition. In accordance with the invention, there are provided the steps of:

delivering a sample of the chemical solution having the first chemical composition to an analysis cell;

performing an ion selective analysis on the chemical solution having the first chemical composition that has been delivered to the analysis cell, said step of performing the ion selective analysis including the further steps of:

delivering a plurality of predetermined amounts of a standard solution having a known concentration of analyte to the chemical solution having the first chemical composition that has been delivered to the analysis cell; and

measuring an electrode potential value of an ion selective electrode responsive to a predetermined chemical characteristic of the chemical solution having the first chemical composition that has been delivered to the analysis cell after delivering each of the predetermined amounts of the standard solution;

determining a quantity of an analyte in the chemical solution having the first chemical composition that has been delivered to the analysis cell, said step of determining a quantity of an analyte including the further step of extrapolating a plurality of the measured electrode potential values back to a predetermined point of analyte concentration.

In one embodiment of this further method aspect of the invention, the step of delivering a plurality of predetermined amounts of extended solution includes delivery of approximately between two and six predetermined amounts of the standard solution. In other embodiments, there is provided the further step of predetermining the amounts of the standard solution having the known concentrations of analyte whereby the in the step of measuring an electro potential value of an ion selective electrode responsive to a predetermined chemical characteristic of the chemical solution having the first chemical composition that has been delivered to analysis cell after delivering each of the predetermined amounts of the standard solution, the electrode potential differences between successive ones of the measurements is approximately between 5 mV and 40

mV. Preferably the electrode potential differences are approximately between 5 mV and 30 mV and the potential differences most preferably are approximately 20 mV.

In a further embodiment of this further method aspect of the invention, there is provided the step of reducing the rate at which the step of delivering a plurality of predetermined amounts of a standard solution is performed. As noted, this will improve the accuracy of determining the endpoint of the titration.

In a further embodiment, the step of extrapolating includes the step of extrapolating a plurality of the measured electro potential values back to the point of zero analyte concentration. In a still further embodiment, the step of delivering the plurality of predetermined amounts of the standard solution having a known concentration of analyte, the concentration of the analyte in the standard solution is high relative to the concentration of the analyte in the chemical solution having the first chemical composition. This reduces the likelihood of diluting the chemical solution having the first chemical composition.

## Brief Description of the Drawing

Comprehension of the invention is facilitated by reading the following detailed description, in conjunction with the annexed drawing, in which:

Fig. 1 is a plan representation of coupling arrangement that is useful in the practice of the invention;

Fig. 2 is a simplified schematic representation of an analyzer arrangement that draws samples from a plurality of chemical tanks;

Fig. 3 is a simplified schematic representation of an arrangement for combining a rinsing solvent with the purge gas arrangement of Fig. 2;

Fig. 4 is a simplified schematic representation of an analyzer/controller embodiment of the invention, showing a control methodology;

Fig. 5 is a simplified schematic diagram of the fluid interconnections between various structural elements of the invention, on a first side of an installation panel;

Fig. 6 is a simplified schematic diagram of certain additional fluid interconnections between various electrical components of the invention; and

Fig. 7 is a simplified schematic diagram of a nitrogen gas circuit, and further showing a stepper motor control board, on a second side of the installation panel shown in Fig. 5.

## Detailed Description

In one aspect of the invention, an analyzer performs sensor differential tracking and alarming. The analysis uses a "differential" endpoint to avoid having to rely on an absolute or calibrated sensor value. When chemical equilibrium is reached during a titration, a large swing in the sensor reading occurs. This difference, or increased rate of change, is what is looked for in order to determine that a titration endpoint is reached. By tracking, reporting, and when necessary, alarming the sensor differential, the user is alerted to potential problems and can elect to perform cleaning or preventative maintenance when necessary.

After being subjected to a calibration process, the system of the present invention analyzes and filters data. Rather than merely accepting an analysis result as true, and then proceeding to employ the result for process control or feedback, a specific illustrative embodiment of the analyzer of the present invention repeats the analysis at least two more times to ensure that the value is repeatable. The result is then checked to determine whether its values are within predetermined ranges, thereby ensuring that the values are reasonable. If the value is repeatable and reasonable, it is accepted as having a high probability of being representative. Several features of the inventive data filtering method are that:

1. the final result is not based simply on the average of many trials;
2. the allowable difference among the trials is restricted to a predeterminable maximum, thereby permitting a selectable accuracy; and
3 the maximum number of trials is limited (usually to nine) so as to terminate unsuccessful attempts and warn the operator of present or impending equipment malfunction.

This methodology both protects the process under control from spurious results as well as provides the user with an indication of the day-to-day performance of the

machine. An increased number of trials to reach a final result is a good warning that maintenance is required.

In accordance with a further aspect of the invention, an automated replenishment volume correction is based upon recipient tank liquid volume. Adjustment of the calculated batch amount advantageously is based upon the current tank level reading.

Safety of the process is enhanced by the implementation of a replenishment volume safety limit. The quantum of replenishment is limited irrespective of the amount indicated by the calculation. In one implementation of this safety feature of the present invention, the analyzer/controller is stepped toward the target replenishment in several increments, particularly if the deviation of the result from the target is large.

In accordance with a still further aspect of the invention, beaker rinsing and filling is effected by means of a high speed, low volume (consumption) spray. The advantageous use of a spray rinse facilitates rapid cleaning and filling of the beaker while requiring only minimal water consumption. In most industries that perform chemical analysis, time and water are critical resources that need to be conserved.

The stirring rate in the titration vessel of the chemical processing system is varied in accordance with established control parameters to achieve maximum mixing and maximum cleaning, while minimizing foaming and air entrapment. The variable stirring rate allows optimization of a variety of functions throughout the titration and cleaning procedure. The titration vessel is sealed, except for a vent/overflow tube that is routed to a drain via an overflow detector. The overflow detector thereby serves to detect and warn of malfunctions.

In a highly advantageous embodiment of the invention, the level in the titration vessel is monitored, or sensed, continuously, rather than by discrete point measurement technique. This enables a more accurate and continuously variable water and reagent delivery and for automated detection of malfunctions. Such problems may include, for example, insufficient reagents, low water pressure, and inoperative valves. By using continuous titration vessel level sensing, it is possible to use simple, low cost valves to deliver and meter liquids into the titration vessel. While this is not of sufficient accuracy

for titrants (*e.g.* ± 0.001 ml), it is sufficient for conditioning reagents or buffers (*e.g.*, ± 0.1 ml).

Pneumatic level detection (*i.e.*, static liquid head pressure against a slowly bubbling immersed tube tip) is used in a titration vessel to achieve continuous level measurement in a confined space containing a broad range of corrosive and caustic solutions. The sensing tube occupies only 0.125" outside diameter size and requires no "head space", *i.e.*, space for apparatus directly above the solution. The tube can be made of any semi-rigid or rigid material that is resistant to the solutions, such as Teflon or glass.

Fig. 1 is a schematic representation of a coupling arrangement 10 that is useful in the practice of the invention. The coupling arrangement uses a threaded element 11 to apply a compression load to a flared portion 13 of a tubing 14. As shown, the distal surface of flared portion 13 is urged sealingly against an elastomer washer seal 15, thereby effecting a connection. It is common in the industry today to use flared tube connections. In known arrangements, the end of a tube (not shown) is flared and literally squeezed between the tip of a threaded nut (not shown) and a hard mating surface (not shown) to create a leak-free connection. The inclusion of chemically resistant elastomer washer 15 between flared portion 13 tube and the mating surface (not shown) improves the coupling by 1) reducing the amount for torque required to form a seal, 2) maintaining the seal in the eventual occurrence of tube material creep or "cold flow," and 3) accommodating minor imperfections in the tubing and mating surfaces. In the practice of this fitting, it is important to employ proper washer diameter and thickness, so as to cause sufficient expansion of the washer when under compression to form a seal, yet not so much as to close off the fluid path through the center of the washer. The proper washer dimensions also facilitate easy and correct alignment (location)) of the washer at installation. It is to be noted that the elastomer washer enjoys a significant performance advantage over conventional Teflon® washers, in that it is not subject to "cold flow," which will eventually cause a leak or require tightening.

Fig. 2 is a simplified schematic representation of an analyzer 20 that illustrates a draw/purge sampling technique that is useful in the practice of the present invention.

Sample fluid provided to analyzers must, of course, be representative of the whole volume in the tank being sampled. To accomplish this samples sometimes are tapped off of a recirculating loop (not shown), usually in the form of a pressurized pipe containing flowing sample. The present analyzer accommodate this, and additionally can draw a sample from a static tank (not shown) several hundred feet away. In the present specific illustrative embodiment of the invention, samples are drawn from three tanks (not shown) via respective ones of valves 22, 23, and 24. The first objective here is to obtain a representative sample. Another objective is to accomplish this with the simplest, or least amount of, equipment. One known solution to this problem is to install a pump (not shown) at the tank and create a further recirculating loop (not shown). This has the drawback of adding a relatively maintenance-intensive piece of equipment, *i.e.*, the pump, and of adding the hazard of constantly recirculating fluid throughout a plant (not shown). Instead of this, the analyzer of the present invention uses a relatively simple eductor 26 to create a vacuum and draw in sample whenever it is required across a sample detector 27. In addition, the unused portion of the sample is afterward blown back to the tank with pressurized air or nitrogen vis a valve 28 to purge the line and prepare for the next draw. In some embodiments of the invention, a pump (not shown) can be used instead of the eductor to create a vacuum to conserve water, which still has the advantage of reduced maintenance requirement due to intermittent use only. Also, in the case of multiple tanks, less equipment in total is required. In a preferred configuration, an analyzer that is equipped to draw samples from several tanks can conserve cost and equipment complexity by utilizing a common vacuum system. Sample that reaches the vacuum system becomes waste. However, sample material that reaches the valves prior to the vacuum system does not become waste product.

The above-described method of sampling also has the benefit of regularly back flushing sample filters (not shown) which may be installed in the sample lines. In conventional systems, sample material flows in only one direction through the filters, thereby causing premature fouling and clogging.

The present inventive method of sampling also has the benefit of assuring that a fresh sample has arrived. Since the sample line is purged with gas after each analysis,

sample detector 27 may be used to confirm the transition from "sample absent" to "sample present." This transition confirms the availability and presence of the sample and the proper operation of the sampling system. By comparison, a recirculating sample system may only have stagnant or unrepresentative sample in it, in which case the mere detection of sample presence is inadequate to ensure a correct analysis result.

Fig. 3 is a simplified schematic representation that shows, in addition to purge gas valve 28 shown in Fig. 2, that a water or solvent rinse valve 29 can be added to clean the system between samplings of incompatible liquids, and to clean the purge gas valve itself. This capability is important because dried sample can otherwise accumulate on this and other valves and cause them to fail. The arrangement of the rinse valve behind the purge gas valve is significant because without it that valve would be especially subject to sample accumulation. This air/water (or gas/solvent) combination is especially efficient at cleaning the apparatus with minimal time and solvent consumption, due the high propulsion and stream breakup caused by the gas. In the practice of the invention, the gas causes what appears as a propelled rain within the tubes.

The three tank sample valves (22, 23, and 24) shown in Fig. 2 can be replaced in certain embodiments of the invention with a single rotary valve (not shown) having multiple inlets and one outlet. This arrangement minimizes "dead legs" and in turn facilitates removal of old sample. This would be particularly advantageous when working with incompatible samples. However, rotary valves can wear easily, causing early valve failure, especially when rotated while full of sample. This vulnerability is overcome by the aforementioned gas/solvent rinse system (Fig. 3), whereby rotary valve rotations can be restricted to periods that the system is clean or empty.

The analyzer of the present invention uses a variable sample volume device, which allows it to accommodate a wide range of sample concentrations and in turn be a more versatile tool by, for example, enabling it to run differing chemistries in series, each requiring a unique sample volume. The sampling device, in the form of a syringe or burette, uses only the middle third of the sample column. This technique prevents both, air in the top third and sediment in the bottom third, from becoming part of the analyzed

sample. This feature is facilitated by the present novel use of the variable volume sampling device.

Waste exits from the titration vessel along a vertical, upward path. This allows for minimum sample mixture entrapment as compared to a horizontal or downward path. The vertical path remains filled with air until it is evacuated with a waste eductor or pump. This is important because trapped liquids can shift or delay titration endpoints.

In the practice of the present invention, the flow of electrolyte is intermittent an controlled. All electrochemical sensors such as pH and ORP require a reference cell, a zero potential electrical connection to the solution. Many schemes have been tried for this, all of them with their benefits and disadvantages. For low maintenance, a gel-filled reference cell electrolyte has been used. The electrolyte does not flow and in turn require refilling, but instead is stagnant. This cell electrolyte however will become poisoned and depleted due to ion migration in and out of the gel and drift over time, becoming non-zero in potential. A known alternative is a slowly flowing electrolyte reference. In this known arrangement, contaminants are flushed out and the zero-potential is maintained. To limit flow and thereby conserve electrolyte, a porous plug of wood, ceramic or plastic is installed at the tip. The disadvantage here is that the pores eventually clog and restrict electrolyte flow and/or cut off the electrical current path, reducing electrode stability and responsiveness.

In the present invention, the flow restricting device is in the form of a valve instead of a porous plug. The valve is located upstream, far from the sample. In this way it cannot clog or impede flow. The electrolyte flow is stagnant during measurements, thus improving stability, and it is allowed to flow briefly during the interval between measurements, thereby maintaining the zero potential junction.

Another feature of the present invention is that the sample tube touches glass beaker wall. This breaks the droplets and allows an exact sample volume to be delivered. The titrant tube tips, on the other hand, are aimed directly into the liquid vortex to minimize mixing time. Additionally, the titration vessel level sensing tube is cut at a 45° angle to minimize signal bounce as bubbles detach.

Fig. 4 is a simplified schematic representation of an analyzer/controller system 40, constructed in accordance with the principles of the invention, that is useful to illustrate a control methodology. As shown in this figure, an analyzer 41, which is integrated with a manager 42, receives a plurality of sample lines, specifically, a sample line 44 from an $H_2O_2$ feed stock drum 48, a sample line 45 from a $H_2O_2$ blend station 49, and a sample line 46 from an $H_2O_2$ distribution tank 50.

The figure additionally shows schematically replenishment controls 52, a local control unit 53 ("LCU 53"), and a level pressure transducer 55. The combination of analyzer 41 and manager 42 effect automatic analysis of a delivered sample under control of LCU 53. The results analysis are displayed, along with a parameter history, replenishment print-outs, system diagnostics, sensor calibration data, and operator alerts and alarms in a display 57. In the event of a malfunction, an alarm 59 is actuated, which incorporates a tower light and an audible signaling arrangement.

A replenisher 60 is schematically indicated in this figure to include a precision syringe pump 62 for effecting automatic replenishment based on the results of the analysis. Replenishment controls 52 are used for multiple chemical delivery destinations from a common pump (not shown). Adjustment of the replenishment is performed under software control in accordance with a predetermined replenishment formula for adjustment that is based on the result of the analysis of $H_2O_2$ replenishment feed stock drum 48.

Level monitoring for distribution tank 50 includes hardware and software for monitoring the level of the distribution tank and adjusting the replenishment volume automatically, as calculated from the analysis. In a specific illustrative embodiment of the invention, the level device at the distribution tank is in the form of a Teflon tubing 64 containing $NO_2$ at approximately between 2 and 10 psi. Distribution of the replenished liquid is effected, in this specific illustrative embodiment of the invention, via a schematically illustrated global supply loop 66, which may be pressurized.

Fig. 5 is a simplified schematic diagram of the fluid interconnections between various structural elements of the invention. As shown, a reaction cell 80, which may be a glass beaker in the practice of the invention, contains a pair of chemical sensors 82 and

83. In one embodiment of the invention, chemical sensor 82 is an ion selective electrode ("ISE") and chemical sensor 83 is a pH sensor or an ORP electrode. Reaction cell 80 is provided with a mixer 85 disposed thereunder.

Deionized water is delivered to the reaction cell from a deionized water source 87 via a valve 88. Valve 88 is an electrically actuated, two-way valve. Delivery of precise quantities of a sample liquid and predetermined reagents is achieved by respective syringe assemblies 90, 91, 92, and 93, which are, in this specific illustrative embodiment of the invention, dedicated to the sample, NaOH, $Ag_2NO_3$, and $Na_2S_2O_3$, respectively. The syringe assemblies are controlled by stepper motors (not shown) that are controlled by the electronics shown in Fig. 7, via respectively associated ones of electric valves 95-98. Purging of syringe assemblies 90, 91, 92, and 93 employs, in this embodiment, nitrogen gas, the rinsing being controllable at a control panel 100. The nitrogen plumbing associated with the operation of control panel 100 is shown in Fig. 7, and will be discussed below.

Waste product is withdrawn from reaction cell 80 by a waste pump 112 (Fig. 6) via an electric valve 110. Fig. 6 is a simplified schematic diagram of certain interconnections between various components of the invention. Elements of structure that previously have been discussed are similarly designated. As shown in this figure, electric valve 110 is connected to waste pump 112.

Sample liquid from sampling chamber 155 is received via lines 116 and 117. Line 117, however, is arranged proximal to a proximity sensor 118 which will issue a signal to a controller (not shown) that indicates that the sample has arrived. The sample then is drawn into syringe assembly 90 via 3-way electrical valve 95.

Fig. 6 further shows a sampling chamber 120 that is connected to a plurality of sample sources 121-125 via respectively associated ones of pneumatic valves 131-135. Each of the pneumatic valves is coupled to an air source 140 via a respectively associated one of electric valves 141-145.

Figs. 5 and 6 show that deionized water from deionized water source 87 is conducted to the top of cell chamber 120 via electric valves 150 and 152. The bottom of cell chamber 120 is coupled to a common line 155 to which sample sources 121-125

are coupled via the respectively associated ones of pneumatic valves 131-135. Common line 155 is coupled to a waste valve 160. In addition, the figures show a grab sample source 161 coupled via an electric valve 163 to common line 155, which as noted, is coupled to the bottom of cell chamber 120. Fig. 5 shows that in this specific illustrative embodiment of the invention, grab sample 161 is drawn from a trough 165.

Fig. 6 illustrates that a KCl electrolyte source 170 is disposed in reagent compartment 171. The KCl electrolyte is supplied to the contents of reaction cell 80 via an electric valve 174. Similarly, a KI source 176 and a $H_2SO_4$ source 177, which also are located in the reagent compartment, are delivered to the reaction cell via respective ones of electric valves 178 and 179. The reagent compartment is also shown to contain a number of reagent sources that are supplied to respective ones of syringe assemblies 90, 91, 92, and 93. These reagents have previously been discussed. Electric valves 95-98 are 3-way valves that are controllable to permit the respectively associated syringe assemblies to take in a respective reagent, or to issue the precisely measured reagent to the reaction cell.

Fig. 7 is a simplified schematic diagram of a nitrogen gas circuit, and further shows a stepper motor control board 180 and other electronic systems for developing electrode signals. Referring to Figs. 5 and 7, a nitrogen source 184 supplies nitrogen to pressure regulators 182 and 183, each of which is connected to an associated one of pressure meters 185 and 186. Pressure regulated nitrogen is conducted from pressure regulator 183 via a line 188 to a T-coupler 190 that is interposed between electric valves 150 and 152. This nitrogen is available to purge sampling chamber 120. A further pressure regulated nitrogen is conducted via a valve 192 and a line 193 to reaction cell 80.

Fig. 7 additionally shows three signal conditioning amplifiers 200, 201, and 202 that are electrically coupled to the ISE, ORP, and pH electrode functions, respectively. in a practical embodiment of the invention, signal conditioning amplifier 200 has an input voltage rating of ±2000 mV; signal conditioning amplifier 201 has an input voltage rating of ±1000 mV; and signal conditioning amplifier 202 has an input voltage rating of 420 mV, with isolated ground. The stepper motors (not shown) that control the syringe

assemblies are themselves controlled via stepper motor control board 180. In this specific illustrative embodiment of the invention, stepper motor control board 180 is capable of controlling four stepper motors.

Although the invention has been described in terms of specific embodiments and applications, persons skilled in the art can, in light of this teaching, generate additional embodiments without exceeding the scope or departing from the spirit of the claimed invention. Accordingly, it is to be understood that the drawing and description in this disclosure are proffered to facilitate comprehension of the invention, and should not be construed to limit the scope thereof.